Triglycerides-based diesel fuels

Anjana Srivastava, Ram Prasad*

Department of Chemical Engineering, H. B. Technological Institute, Kanpur, 208002, India

Abstract

Efforts are under way in many countries, including India, to search for suitable alternative diesel fuels that are environment friendly. The need to search for these fuels arises mainly from the standpoint of preserving the global environment and the concern about long-term supplies of conventional hydrocarbon-based diesel fuels. Among the different possible sources, diesel fuels derived from triglycerides (vegetable oils/animal fats) present a promising alternative to substitute diesel fuels. Although triglycerides can fuel diesel engines, their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as biodiesel, derived from triglycerides by transesterification with methanol have received the most attention. The main advantages of using biodiesel are its renewability, better-quality exhaust gas emissions, its biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Diesel fuels have an essential function in the industrial economy of a country. These are used in heavy trucks, city transport buses, locomotives, electric generators, farm equipment, underground mine equipment, etc. Compared to the rest of the world, India's demand for diesel fuels is roughly six times that of gasoline. The consumption of diesel fuels in India in 1994–95 was 28.30 million tonnes which was 43.2% of the total consumption of petroleum products. This

* Corresponding author. Tel.: +91-294851-55; fax: +91-0512-545312.

Table 1
Important characteristics of diesel fuels

Fuel characteristics	Comments
Cetane number	(a) A measure of ignition quality of diesel fuels (b) High cetane number implies short ignition delay (c) Higher molecular weight normal alkanes have high cetane numbers (d) Influences both gaseous and particulate emissions (e) Cetane index which is very close to cetane number is calculated based on 10, 50, 90% distillation temperatures and specific gravity (f) Fuels with high autoignition temperatures are more likely to cause diesel knock
Distillation range	(a) Affects fuel performance and safety (b) Important to an engine's start and warm up (c) Presence of high-boiling components affect the degree of formation of solid combustion deposits (d) Needed in the estimation of cetane index
Specific gravity	(a) Required for the conversion of measured volumes to volumes at standard temperature of 15°C (b) Used in the calculation of cetane index
Heat of combustion	(a) A measure of energy available in a fuel (b) A critical property of fuel intended for use in weight-limited vehicles
Flash point	(a) Indicates the presence of highly volatile and flammable materials (b) Measures the tendency of oil to form a flammable mixture with air (c) Used to assess the overall flammability hazard of a material
Viscosity	(a) Proper viscosity of fuel required for proper operation of an engine (b) Important for flow of oil through pipelines, injector nozzles and orifices (c) Effective atomization of fuel in the cylinder requires limited range of viscosity of the fuel to avoid excessive pumping pressures
Contamination (water/ sediment)	(a) Causes corrosion of equipment (b) Causes problems in processing (c) Required to accurately measure net volumes of actual fuel in sales, taxation, exchanges and custody transfer
Copper-strip corrosion	(a) A measure to assess relative degree of corrosivity (b) Indicates the presence of sulphur compounds
Cloud point, pour point cold-filter plugging point	(a) A measure of the performance of fuels under cold temperature conditions (b) Used as quality control specification or low temperature handling indicators for large storage tanks and pipelines at refineries and terminals
Carbon residue	(a) Correlates with the amount of carbonaceous deposits in the combustion chamber (b) Greater carbon deposits expected for higher values of carbon residue
Particulate matter	(a) Indicates the potential of emission of particulate matter (b) Contains primarily carbon particles (c) Soot (carbonaceous particulates formed from gas-phase processes) particles absorb and carry carcinogenic materials into environment as emission and can cause an ill effect on human health. Excessive soot particles might clog the exhaust valves

Table 1 (*continued*)

Fuel characteristics	Comments
Ash	(a) Results from oil, water-soluble metallic compounds or extraneous solids, such as dirt and rust
	(b) Can be used to decide product's suitability for a given application
Sulphur	(a) Controlled to minimize corrosion, wear and tear
	(b) Causes environmental pollution from their combustion products
	(c) Corrosive in nature and causes physical problems to engine parts

requirement was met by importing crude petroleum as well as petroleum products. The import bill on these items was Rs. 17,838 crores. With the expected growth rate of diesel consumption of more than 14% per annum, shrinking crude oil reserves and limited refining capacity, India will be heavily dependent on imports of crude petroleum and petroleum products. Moreover, some recent estimates of worldwide petroleum reserves predict them to last only 45 years.

From the standpoint of preserving the global environment and the concern regarding long-term supplies of conventional hydrocarbon-based diesel fuels, it is logical that research and development on different possible sources of petroleum products should be carried on with the special emphasis on yield and quality of diesel fuels.

2. Hydrocarbon-based diesel fuels

It is a general property of hydrocarbons that the auto-ignition temperature is higher for more volatile hydrocarbons. Therefore, the less volatile middle distillate fractions of crude oil boiling in the range of 250 to 370°C are suitable as diesel fuels. The hydrocarbons present in the diesel fuels include paraffins, naphthenes, olefins and aromatics. Carbon numbers of these hydrocarbons ranges from 12 to 18. Since straight-run diesel fraction from a given crude oil is fixed, varying amounts of selected cracked distillates from conversion processes such as fluid catalytic cracking, hydrocracking, coking units are used to increase the volume available for meeting the growing demand of diesel fuels.

The important characteristics of diesel fuels are listed in Table 1 [1,2]. Indian requirements of diesel fuels are listed in Table 2. The performance problems versus fuel-related causes for compression–ignition (diesel) engines are summarised in Table 3 [3]. The more critical problems are those related to combustion, injector nozzle/pump fouling and filter plugging.

3. Alternative diesel fuels

The alternative diesel fuels must be technically acceptable, economically competitive, environmentally acceptable and easily available. From the viewpoint

Table 2
Indian requirements for diesel fuels IS:1460–1974

Sl. No.	Characteristics	Requirement
1	Acidity, inorganic	Nil
2	Acidity, total, mg KOH/g, Max.	0.50
3	Ash, wt.%, Max.	0.01
4	Carbon residue (Ramsbottom), wt.%, Max.	0.20
5	Cetane number, Min.	42.00[b]
6	Pour point, °C, Max.	6.00[a]
7	Copper strip corrosion for 3 h at 100°C	Not worse than No. 1
8	Distillation-recovery at 366°C, vol.%, Min.	90.00
9	Flash point (Abel), °C, Min.	38.00
10	Kinematic viscosity at 38°C, cSt	2.0–7.5
11	Sediment, wt.%, Max.	0.05
12	Total sulphur, wt.%, Max.	1.00
13	Water content, vol.%, Max.	0.05

[a] Subject to seasonal changes, pour point varies from 0 to 18°C.
[b] 45 for Naval applications.

Table 3
Effect of performance of fuel on compression–ignition engine

Performance problem	Probable fuel-related causes
1. Poor combustion, smoking	(a) Low cetane number
	(b) Water contamination
	(c) Improper cloud point
	(d) Lighter/heavier fuel contamination
2. Excess cylinder wear	(a) Fuel dilution
	(b) High sulphur content
	(c) Dirt (silicon) contamination
3. Injector nozzle plugging/wear	(a) Soluble metal contaminants
	(b) Heavy end impurities
	(c) Preformed gum impurities
4. Injector pump fouling sticking	(a) High sulphur/hetero-atom content
	(b) Heavy ends contamination
	(c) Gasoline contamination
	(d) Low fuel viscosity
5. Filter plugging	(a) Water contamination
	(b) Fuel impurities
	(c) Improper cloud point
	(d) Thermally-reactive hydrocarbons
6. Excess engine deposits	(a) Heavy ends contamination
	(b) Low cetane number
	(c) High sulphur/hetero-atom content

of these requirements, triglycerides (vegetable oils/animal fats) and their derivatives may be considered as viable alternatives for diesel fuels. Vegetable oils are widely available from a variety of sources, and they are renewable. As far as

environmental considerations are concerned, unlike hydrocarbon-based fuels, the sulphur content of vegetable oils is close to zero and hence, the environmental damage caused by sulphuric acid is reduced. Moreover, vegetable oils take away more carbon dioxide from the atmosphere during their production than is added to it by their later combustion. Therefore, it alleviates the increasing carbon dioxide content of the atmosphere.

4. Triglycerides as diesel fuels

The use of vegetable oils, such as palm, soya bean, sunflower, peanut and olive oils as alternative fuels for diesel engines dates back almost nine decades. Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is again promoted in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soya bean oil in the United States, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in The Philippines are being considered as substitutes for diesel fuels. The production of oilseeds in India is given in Table 4 [4]. This indicates that the use of vegetable oils as the source of diesel fuels in India requires additional steps to increase the production of oilseeds. It is also necessary to develop new and more productive plant sources whose seeds have high oil content.

4.1. Composition of vegetable oils

The basic constituent of vegetable oils is triglyceride. Fig. 1 shows a typical triglyceride molecule. Vegetable oils comprise 90 to 98% triglycerides and small

Table 4
Production of oilseeds in 1995–96

Oilseed	Production, million tonnes	
	World	India
Soya bean	123.2	4.50
Cottonseed	34.3	4.71
Groundnut	19.3	5.12
Sunflower	25.2	1.40
Rapeseed	34.7	6.10
Sesame	2.5	0.90
Palm kernels	4.8	–
Copra	4.9	0.50
Linseed	2.6	0.30
Castor	1.3	0.90
Total	252.8	24.40

$$
\begin{array}{c}
\overset{\displaystyle O}{\overset{\displaystyle \|}{H_2C\text{-}O\text{-}C}}\text{-}(CH_2)_{16}CH_3 \\[3em]
\overset{\displaystyle O}{\overset{\displaystyle \|}{HC\text{-}O\text{-}C}}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\[3em]
\overset{\displaystyle O}{\overset{\displaystyle \|}{H_2C\text{-}O\text{-}C}}\text{-}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3
\end{array}
$$
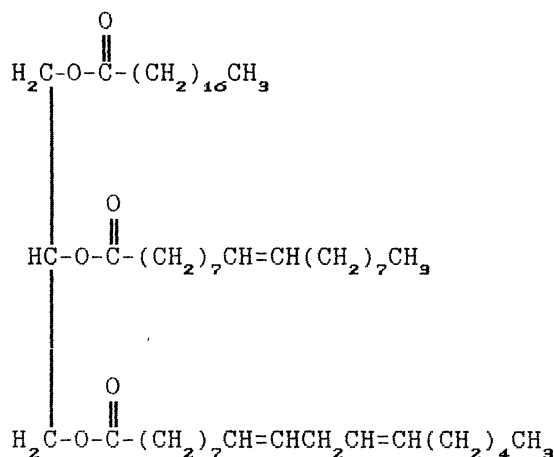
Fig. 1. Structure of a typical triglyceride molecule.

amounts of mono- and diglycerides. Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amounts of oxygen in its structure. Fatty acids vary in their carbon chain length and in the number of double bonds. The structures of common fatty acids are given in Table 5 [5]. Tables 6a and b summarize the fatty acid composition of some vegetable oils [6,7]. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water [5].

4.2. Fuel-related properties of vegetable oils

The fuel-related properties of vegetable oils are listed in Table 7 [6,8]. The kinematic viscosity of vegetable oils varies in the range of 30 to 40 cSt at 38°C. High viscosity of these oils is due to large molecular mass and chemical structure. Vegetable oils have high molecular weights in the range of 600 to 900, which are three or more times higher than diesel fuels. The flash point of vegetable oils are very high (above 200°C). The volumetric heating values of these oils are in the range of 39 to 40 MJ/kg which are low compared to diesel fuels (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The cetane numbers are in the range of 32 to 40. The iodine value ranges from 0 to 200 depending upon unsaturation. The cloud and pour points of vegetable oils are higher than that of diesel fuels.

4.3. Performance of vegetable oils as diesel fuels

It has been found that the use of vegetable oils as diesel fuels in conventional diesel engines leads to a number of problems which are related to the type and

Table 5
Chemical structure of common fatty acids

Fatty acid	Systematic name	Structure[a]	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	*cis*-13-Docosenoic	22:1	$C_{22}H_{42}O_2$

[a] *xx:y* indicates *xx* carbons in the fatty acid chain with *y* double bonds.

Table 6a
Chemical composition of vegetable oils[a]

Vegetable oil	Fatty acid composition, wt.%									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O. Safflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

[a] Tr = traces.

Table 6b
Chemical composition of vegetable oils

Vegetable oil	Fatty acid composition, wt.%						
	14:0	16:0	18:0	20:0	24:0	18:1	18:2
Rice-bran	0.4–0.6	11.7–16.5	1.7–2.5	0.4–0.6	0.4–0.9	39.2–43.7	26.4–35.1
Sal	–	4.5–8.6	34.2–44.8	6.3–12.2	–	34.2–44.8	2.7
Mahua	–	16.0–28.2	20.0–25.1	0.0–3.3	–	41.0–51.0	8.9–13.7
Neem	0.2–0.26	13.6–16.2	14.4–24.1	0.8–3.4	–	49.1–61.9	2.3–15.8
Karanjia	–	3.7–7.9	2.4–8.9	–	1.1–3.5	44.5–71.3	10.8–18.3

Table 7
Properties of vegetable oils

Vegetable oil	Kinematic viscosity at 38°C mm²/s	Cetane number	Heating value MJ/kg	Cloud point °C	Pour point °C	Flash point °C	Density kg/l	carbon residue wt.%	Ash wt.%	Sulphur wt.%
Corn	34.9	37.6	39.5	−1.1	−40.0	277	0.9095	0.24	0.010	0.01
Cottonseed	33.5	41.8	39.5	1.7	−15.0	234	0.9148	0.24	0.010	0.01
Crambe	53.6	44.6	40.5	10.0	−12.2	274	0.9044	0.23	0.050	0.01
Linseed	27.2	34.6	39.3	1.7	−15.0	241	0.9236	0.22	< 0.010	0.01
Peanut	39.6	41.8	39.8	12.8	−6.7	271	0.9026	0.24	0.005	0.01
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115	0.30	0.054	0.01
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144	0.25	0.006	0.01
H.O. Safflower	41.2	49.1	39.5	−12.2	−20.6	293	0.9021	0.24	< 0.001	0.02
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133	0.25	< 0.010	0.01
Soya bean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138	0.27	< 0.010	0.01
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161	0.23	< 0.010	0.01
Palm	39.6	42.0	–	31.0	–	267	0.9180	–	–	–
Babassu	30.3	38.0	–	20.0	–	150	0.9460	–	–	–
Tallow	–	–	40.0	–	–	201	–	6.21	–	–

grade of oil and local climatic conditions [9,10]. The injection, atomization and combustion characteristics of vegetable oils in diesel engines are significantly different from those of hydrocarbon-based diesel fuels. The high viscosity of vegetable oils interferes with the injection process and leads to poor fuel atomization. The inefficient mixing of oil with air contributes to incomplete combustion. The high flash point attributes to its lower volatility characteristics. This leads to more deposit formation, carbonization of injector tips, ring sticking and lubricating oil dilution and degradation. The combination of high viscosity and low volatility of vegetable oils causes poor cold engine start up, misfire and ignition delay. Oxidative and thermal polymerisation of vegetable oils cause a deposition on the injectors forming a film that will continue to trap fuel and interfere with combustion. In the long-term operation, vegetable oils normally develop gumming, injector coking and ring sticking. Another problem is incompatibility with conventional diesel fuels. Therefore, the engine must be more or less modified according to the conditions of use and the oil involved. The modified engines built by Elsbett in Germany and Malaysia and Diesel Morten und Geraetebau GmbH (DMS) in Germany and in the USA show a good performance when fuelled with vegetable oils of different compositions and grades.

5. Derivatives of triglycerides as diesel fuels

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon-based diesel fuels. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. These can be changed in at least four ways:

- pyrolysis;
- microemulsification;
- dilution; and
- transesterification.

5.1. Pyrolysis

Pyrolysis refers to a chemical change caused by the application of thermal energy in the presence of air or nitrogen sparge. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engines. These studies include the effect of temperature on the type of products obtained, the use of catalysts, largely metallic salts, to obtain paraffins and olefins similar to those present in hydrocarbon-based diesel fuels, the characterization of the thermal decomposition products.

Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different

types of vegetable oils produce large differences in the composition of the thermally decomposed oil. Fig. 2 outlines a schematic that accounts for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from pyrolysis of triglycerides. Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism. Formation of homologous series of alkanes and alkenes is accountable from the generation of the RCOO radical from the triglyceride cleavage and subsequent loss of carbon dioxide. The R radical, upon disproportionation and ethylene elimination, gives the odd-numbered carbon alkanes and alkenes. The presence of unsaturation enhances cleavage at a position α, β to the unsaturation. Thermal positional isomerization and subsequent cleavage could account for the higher amounts of C_5 to C_{10} alkanes obtained from safflower compared with soya bean oil. The formation of aromatics is supported by a Diels–Alder addition of ethylene to a conjugated diene formed in the pyrolysis reaction. Carboxylic acids formed during the pyrolysis of vegetable oils probably result from cleavage of the glyceride moiety.

The liquid fractions of the thermally decomposed vegetable oil is likely to approach diesel fuels. The pyrolysed soya bean oil contains 79% carbon and
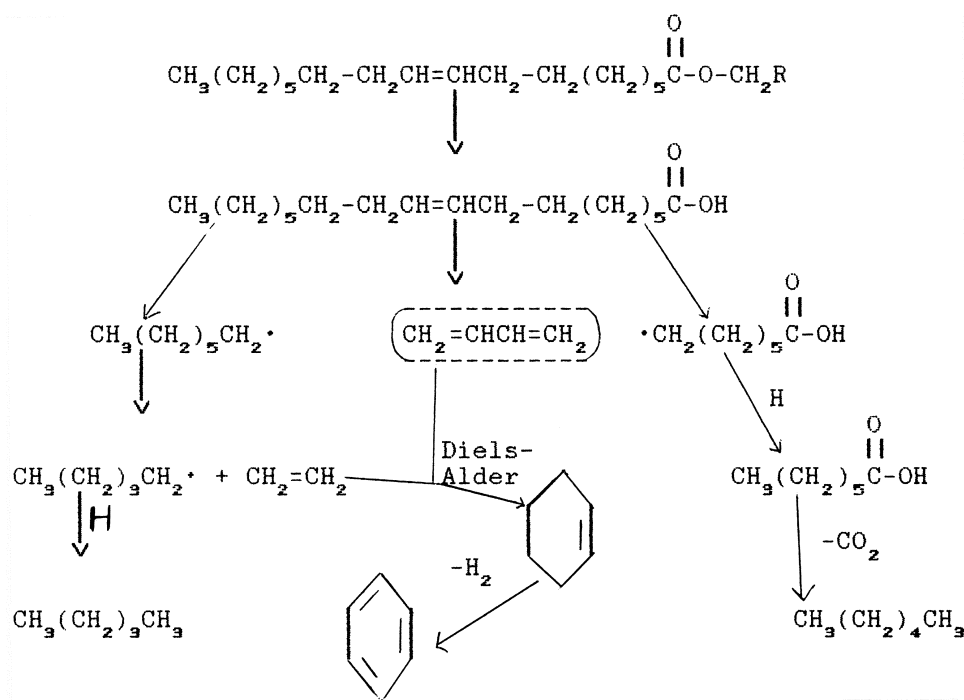

Fig. 2. Thermal decomposition mechanisms.

11.88% hydrogen [11]. It has low viscosity and a high cetane number compared to pure vegetable oils. The cetane number of pyrolysed soya bean oil is enhanced to 43 from 37.9 and the viscosity is reduced to 10.2 cSt from 32.6 at 38°C [11,12], but it exceeds the specified value of 7.5 cSt. The pyrolysed vegetable oils possess acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue amounts and pour point. Engine testing on pyrolysed oil has been limited to short-term tests.

5.2. Microemulsification

Microemulsions are isotropic, clear, or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called cosurfactant [12,13]. The droplet diameters in microemulsions range from 100 to 1000 Å. A microemulsion can be made of vegetable oils with an ester and dispersant (cosolvent), or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels. Microemulsions because of their alcohol content have lower volumetric heating values than diesel fuels, but the alcohols have high latent heat of vaporization and tend to cool the combustion chamber, which would reduce nozzle coking. A microemulsion of methanol with vegetable oils can perform nearly as well as diesel fuels. The use of 2-octanol as an effective amphiphile in the micellar solubilization of methanol in triolein and soya bean oil has been demonstrated [12]. The viscosity was reduced to 11.2 cSt at 25°C. The reported engine tests on a microemulsion consisting of soya bean oil:methanol:2-octanol:cetane improver (52.7:13.3:33.3:1) indicate the accumulation of carbon around the orifices of the injector nozzles and heavy deposits on exhaust valves.

5.3. Dilution

Dilution of vegetable oils can be accomplished with such materials as diesel fuels, a solvent or ethanol. The dilution of sunflower oil with diesel fuels in the ratio of 1:3 by volume has been studied and engine tests were carried out by Ziejewski et al. [10]. The viscosity of this blend was 4.88 cSt at 40°C. They concluded that the blend could not be recommended for long-term use in the direct injection diesel engines because of severe injector nozzle coking and sticking. A comparable blend with high oleic safflower oil was also tested and it gave satisfactory results, but its use in the long term is not applicable as it leads to thickening of lubricant. A 1:1 blend of soya bean oil and stoddard solvent (48% paraffins and 52% naphthenes) had viscosity of 5.12 cSt at 38°C. This fuel produced heavy carbon deposit on the tulips of the intake valves and showed considerable top ring wear.
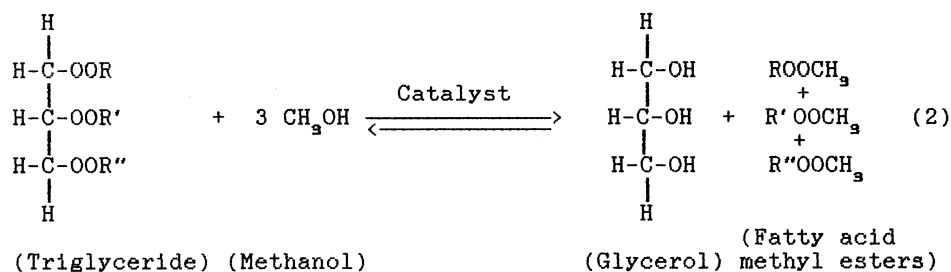
5.4. Transesterification

Transesterification [14], also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than an

alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides. The transesterification reaction is represented by the general equation:

$$RCOOR' + R''OH \overset{\text{Catalyst}}{\rightleftarrows} RCOOR'' + R'OH$$

Ester   Alcohol   Ester   Alcohol   (1)
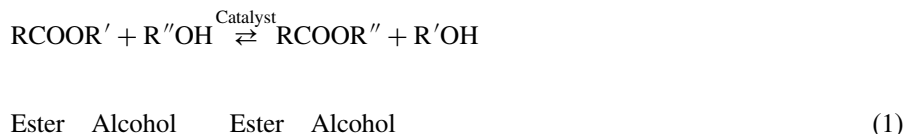
If methanol is used in the above reaction, it is termed methanolysis. The reaction of triglyceride with methanol is represented by the general equation:

$$
\begin{array}{lcl}
\begin{array}{l}
\text{H} \\
| \\
\text{H-C-OOR} \\
| \\
\text{H-C-OOR'} \\
| \\
\text{H-C-OOR''} \\
| \\
\text{H}
\end{array}
&
\begin{array}{c}
+ \quad 3\ CH_3OH \quad \xrightarrow{\text{Catalyst}}
\end{array}
&
\begin{array}{l}
\text{H} \\
| \\
\text{H-C-OH} \quad ROOCH_3 \\
| \qquad\qquad\quad + \\
\text{H-C-OH} + R'OOCH_3 \quad (2) \\
| \qquad\qquad\quad + \\
\text{H-C-OH} \quad R''OOCH_3 \\
| \\
\text{H}
\end{array}
\end{array}
$$

(Triglyceride) (Methanol)   (Glycerol) (Fatty acid methyl esters)

The fatty acid methyl esters (known as biodiesel) are attractive as alternative diesel fuels. The details on biodiesel are given below.

6. Biodiesel

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as vegetable oils or animal fats, for use in compression–ignition (diesel) engines [15]. The biodiesel that is considered as a possible substitute or extender of conventional diesel fuel is commonly composed of fatty acid methyl esters that are prepared from the triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Biodiesel is compatible with conventional diesel and the two can be blended in any proportion. A number of units are manufacturing biodiesel worldwide. These units are using sunflower oil, used-frying oil, jatropha oil, etc. as a source of triglycerides. Table 8 gives the global production of biodiesel [15].

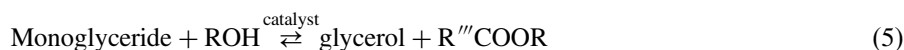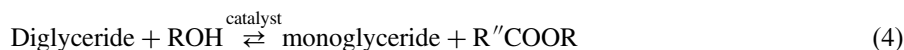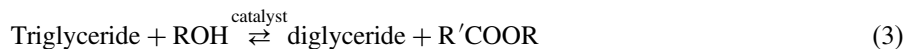### 6.1. Chemistry of transesterification process

The overall transesterification reaction is given by Eq. (2). However, three consecutive and reversible reactions are believed to occur. These reactions are

Table 8
Global production of biodiesel

Country	Number of plants[a]	Location	Total annual capacity, tonnes	Oils used
Austria	11(1)	Aschach, Bruck, Pischelsdorf	56,200–60,000	Used-frying oil
Belgium	3	Feluy, Seneffe	241,000	–
Canada	1	Saskatoon		
Czechoslavakia	17(1)	Mydlovary, Olomouc	42,500–45,000	Used-frying oil
Denmark	3	Otterup, Jutland	32,000	–
France	7(1)	Rouen, Compiegne, Boussens, Peronne, Verdun, Nogentsurseine	38,100	–
Germany	8(4)	Leer, Dusseldorf, Kiel, Barby, Germunden, Thuringia	207,000	–
Hungary	17(16)	Visnye, Gyor	18,880	–
Ireland	1	–	5000	Used-frying oil
Italy	9(4)	Livomo, Cittadi, Casleto, Milano, Solbiate, Napoli, Bari, Ancona, Brescia	779,000	Sunflower oil
Nicaragua	1	–	–	Jatropha oil
Slovak Republic	10(1)	Barcelona	50,500–51,500	–
Spain	1	Bilbao	500	–
Sweden	3(1)	Gothenborg, Skane, Orebro	75,000	–
Switzerland	1	Geneva	2000	–
U.K.	1	East Dusham	–	–
U.S.A.	4(3)	Midwest, Chicago, Quincy	190,000	Used-frying oil
Yugoslavia	2	–	5000	–

[a] Figure within parenthesis indicates the number of plants under construction.

given below:

$$\text{Triglyceride} + \text{ROH} \overset{\text{catalyst}}{\rightleftarrows} \text{diglyceride} + \text{R}'\text{COOR} \tag{3}$$

$$\text{Diglyceride} + \text{ROH} \overset{\text{catalyst}}{\rightleftarrows} \text{monoglyceride} + \text{R}''\text{COOR} \tag{4}$$

$$\text{Monoglyceride} + \text{ROH} \overset{\text{catalyst}}{\rightleftarrows} \text{glycerol} + \text{R}'''\text{COOR} \tag{5}$$

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step [16,17].

6.2. Properties of biodiesel

The properties of biodiesel and diesel fuels are compared in Table 9 [8,9,18–20].

Table 9
Properties of biodiesel

Vegetable oil methyl ester	Kinematic viscosity at 37.8°C mm^2/s	Cetane number	Lower heating value MJ/l	Cloud Point °C	Pour point °C	Flash point °C	Density gm/ml	Carbon residue wt.%	Copper strip corrosion
Peanut	4.9	54	33.6	5	–	176	0.883	–	–
Soya bean	4.5	45	33.5	1	–7	178	0.885	1.74	1a
Babassu	3.6	63	31.8	4	–	127	0.879	–	–
Palm	5.7	62	33.5	13	–	164	0.880	–	–
Sunflower	4.6	49	33.5	1	–	183	0.860	–	–
Tallow	–	–	–	12	9	96	–	1.83	1a

The characteristics of biodiesel are close to diesel fuels, and therefore biodiesel becomes a strong candidate to replace the diesel fuels if the need arises. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third that of the triglyceride, reduces the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to diesel fuels. These esters contain 10 to 11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine. The cetane number of biodiesel is around 50. The use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties. Since the volatility increases marginally, the starting problem persists in cold conditions. Biodiesel has lower volumetric heating values (about 12%) than diesel fuels but has a high cetane number and flash point. The esters have cloud point and pour points that are 15 to 25°C higher than those of diesel fuels.

6.3. Methods of manufacture

Different technologies are currently available and used in the industrial production of biodiesel, which is sold under different trademarks. For example, there are the Italian processes Novamont and Ballestra, the French IFP, the German Henkel and ATT.

Biodiesel is manufactured by the transesterification of fats and oils. Triglycerides are readily transesterified batchwise in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60 to 70°C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower glycerine layer is drawn off while the upper methyl ester layer is washed to remove entrained glycerine and is then processed further. The excess methanol is recovered in the condenser, sent to a rectifying column for purification and recycled.

The Henkel process [21] operates at 9000 kPa and 240°C and uses unrefined oil as feedstock. Unrefined oil, methanol in excess and catalyst are metered and heated to 240°C before feeding into the reactor. The bulk of the excess methanol is flashed off as it leaves the reactor and is fed to a bubble tray column for purification. The recovered methanol is recycled into the system. The mixture from the reactor enters a separator where the glycerine in excess of 90% concentration is removed. The methyl ester is subsequently fed to a distillation column for purification. Further fractionation into special cuts may follow if desired.

The Lurgi process [21] operates at normal pressure. This process requires the use of a degummed and deacidified feedstock. The refined vegetable oil and methanol are reacted in a two-stage mixer-settler arrangement in the presence of a catalyst. The glycerine produced in the reaction, dissolved in the surplus methanol, is recovered in the rectification column. Most of the entrained methanol

and glycerine are recovered from the methyl ester in the countercurrent scrubber. The methyl ester can be further purified by distillation.

6.4. Process variables

The most important variables that influence transesterification reaction time and conversion are [22]:

- reaction temperature;
- ratio of alcohol to oil;
- catalyst type and concentration;
- mixing intensity;
- purity of reactants.

6.4.1. Reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60 to 70°C) at atmospheric pressure. These mild reaction conditions, however, require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, the degummed and deacidified feedstock is used at these conditions. The pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240°C). Under these conditions, simultaneous esterification and transesterification take place [21]. The maximum yield of esters occurs at temperatures ranging from 60 to 80°C at a molar ratio (alcohol to oil) of 6:1 [18,23]. Further increase in temperature is reported to have a negative effect on the conversion. The butanolysis and methanolysis of soya bean oil were studied at different temperatures in the presence of acidic and alkaline catalysts. These studies indicated that given enough time, transesterification can proceed satisfactorily at ambient temperatures in the case of the alkaline catalyst [16].

6.4.2. Ratio of alcohol to oil

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to yield 3 mol of fatty esters and 1 mol of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred wherever feasible, since in this way, the reaction can be driven to completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight. Krisnangkura and Simamaharnnop [24] transmethylated palm oil at 70°C in an organic solvent (toluene) with sodium methoxide as catalyst and

stated that the conversion increases with increase in molar ratio of methanol to palm oil. However, higher molar ratio of alcohol to vegetable oil interferes in the separation of glycerol.

6.4.3. Catalyst type and concentration

Alkali metal alkoxides are the most effective transesterification catalyst compared to the acidic catalyst. Sodium alkoxides are among the most efficient catalysts used for this purpose, although KOH and NaOH can also be used. Transmethylations occur approximately 4000 times faster in the presence of an alkaline catalyst than those catalysed by the same amount of acidic catalyst [25]. Partly for this reason and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterifications are conducted with alkaline catalysts. The alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion of vegetable oil into esters [18,24]. Further, increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove it from the reaction medium at the end.

It has been shown that lipases are able to catalyze the alcoholysis of triglycerides in both aqueous and nonaqueous systems [26–28]. The reaction follows Michaelis Menten kinetics and enzymatic kinetics agree with a Ping-pong Bi–Bi mechanism. Haas and Scott [29] studied the feasibility of using diesel fuel as a solvent for the enzymatic synthesis of ethyl esters from triglycerides and a phospholipid. This suggests the possibility of applying this reaction to the synthesis of biodiesel from low-value materials such as soapstock, which are rich in these lipids and in related compounds.

6.4.4. Mixing intensity

In the transesterification reaction, the reactants initially form a two-phase liquid system. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant. The understanding of the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale-up and design.

6.4.5. Purity of reactants

Impurities present in the oil also affect conversion levels. Under the same conditions, 67 to 84% conversion into esters using crude vegetable oils can be obtained, compared with 94 to 97% when using refined oils. The free fatty acids in the original oils interfere with the catalyst. However, under conditions of high temperature and pressure this problem can be overcome.

6.5. Quality specifications of biodiesel

Table 10 provides the German standard for biodiesel [30]. This standard includes properties such as density at 15°C, kinematic viscosity at 40°C, flash point, cold-filter plugging point, cetane number, carbon residue (10% distillation), iodine number. Similar standards for the use of biodiesel as diesel fuels are being followed in Austria, Italy and other European countries. In Germany, the use of rapeseed oil methyl esters as fuel in a series of vehicles is in practice. A similar approval is expected in Southeast Asia for the use of palm oil methyl esters followed by the United States where trials have been performed on soya bean oil methyl esters.

6.6. Performance of biodiesel

The conventional diesel engine can be operated with biodiesel without much modification in the engine [31]. Compared to hydrocarbon-based diesel fuels, the higher cetane number of biodiesel results in shorter ignition delay and longer combustion duration and hence, low particulate emissions. Biodiesel exhaust has a

Table 10
Biodiesel standard DIN V51606 (Germany)

Properties	Limits	
	Minimum	Maximum
1. Density at 15°C, g/ml	0.875	0.90
2. Kinematic viscosity at 40°C, mm^2/s	3.500	5.00
3. Flash point (Pensky–Martens), °C	100.000	
4. Cold filter plugging point, °C		
15 April–30 September		0.00
1 October–15 November		−10.00
16 November–28 February		−20.00
1 March–14 April		−10.00
5. Sulphur content, wt.%		0.01
6. Carbon residue, wt.% (10% distillation)		0.30
7. Cetane number		49.00
8. Ash, wt.%		0.01
9. Water, mg/kg		300.00
10. Total dirt, mg/kg		20.00
11. Copper corrosion for 3 h at 50°C		1.00
12. Neutralization number, mg KOH/g		0.50
13. Methanol, wt.%		0.30
14. Monoglycerides, wt.%		0.80
15. Diglycerides, wt.%		0.10
16. Triglycerides, wt.%		0.10
17. Free glycerol, wt.%		0.02
18. Iodine number, g Iodine/100 g		115.00
19. Phosphorous, mg/kg		10.00

less offensive odour. Its use results in the minimization of carbon deposits on injector nozzles. It has been reported that if an engine is to be operated on biodiesel for a long time, then the injection timing can be readjusted to obtain better thermal efficiency [9]. Biodiesel has been used in blends with hydrocarbon-based diesel fuels. The most popular blend contains 20% biodiesel. Several studies have shown that diesel/biodiesel blends reduce smoke opacity, particulates, unburnt hydrocarbons, carbon dioxide and carbon monoxide emissions, but nitrous monoxide emissions are slightly increased. One limitation to the use of biodiesel is its tendency to crystallize at low temperatures below 0°C. Methyl and ethyl esters of vegetable oils will crystallize and separate from diesel at temperatures often experienced in winter time operation. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation. One solution to this problem may be the use of branched-chain esters, such as isopropyl esters [32]. The isopropyl esters of soya bean oil crystallize 7 to 11°C lower than the corresponding methyl esters. Another method to improve the cold flow properties of vegetable oil esters is to remove high-melting saturated esters by inducing crystallization with cooling, a process known as winterization. This process depresses the cloud point of esters by equilibrating them at temperatures below their cloud point and above their pour point over an extended period of time, then filtering away the solids [33,34]. Winterization can reduce the cloud point of methyl soyate to −16°C. The effect of cold-flow additives on cloud point, pour point, cold-filter plugging point (CFPP) and low-temperature flow test (LTFT) have been studied by Dunn et al. [34]. The additive treatment significantly improves the pour point of distillate/methyl ester blends. However, additives do not greatly affect cloud point. Both CFPP and LTFT are nearly linear functions of cloud point. Additives reduce LTFT of neat methyl esters by 5 to 6°C.

The problems encountered in the long-term storage of biodiesel are mainly due to hydrolytic and oxidative degradation. Hydrolytic degradation consists of hydrolysis of methyl esters when water is present in the reaction medium. It can be influenced by the initial acid content of the product, which has a catalytic effect on the above mentioned reaction, the quantity of water actually present (dissolved, emulsified or separated at the bottom of the vessel). The solubility and the emulsifiability in water of this fuel are heavily dependent on the quality of the product. In particular, a biodiesel with a high content of intermediate reaction products (mono- and diglycerides) will have the tendency to absorb water, with all the associated negative effects, to a higher degree than a biodiesel that is constituted mainly of methyl esters. Oxidative degradation develops from hydroperoxide toward secondary oxidation products. It is influenced by the nature of the original fatty substance (in terms of number of double bonds), by its quality with particular reference to the presence of hydroperoxides and natural antioxidants, by the presence of pro-oxidizing agents (such as ultraviolet light and some metals), and by temperature and air. Bondioli et al. [35] studied the behaviour of rapeseed oil methyl ester under controlled storage conditions that simulate those found in reality. They observed storage behaviour at a temperature of 20 and 40°C in the presence of different quantities of water in iron and glass

containers and reported acid and peroxide values for a period of 180 days. The path of oxidation of rapeseed oil methyl ester is strongly influenced by the characteristics of the storage container and by temperature.

6.7. Economical feasibility of biodiesel

India has rich and abundant forest resources with a wide range of plants and oilseeds. The production of these oilseeds can be stepped up many fold if the government takes the decision to use them for producing diesel fuels. Economical feasibility of biodiesel depends on the price of the crude petroleum and the cost of transporting diesel long distances to remote markets in India. It is certain that the cost of crude petroleum is bound to increase due to increase in its demand and limited supply. Further, the strict regulations on the aromatics and sulphur contents in diesel fuels will result in higher cost of production of diesel fuels as removal of aromatics from the distillate fractions requires capital-intensive processing equipment and continuous high cost operations because of the large amounts of hydrogen required for the ring saturation. Similarly, decreasing the sulphur content is also a big challenge to the refiner. The proposed changes in Indian diesel specification include total aromatics content up to 25 vol.% (maximum) and sulphur reduction from 1 to 0.5 wt.% (maximum) by the year 2005.

The cost of producing methyl or ethyl esters from edible oils is currently much more expensive than hydrocarbon-based diesel fuels. Due to the relatively high costs of vegetable oils (about four times the cost of diesel in India), methyl esters produced from it cannot compete economically with hydrocarbon-based diesel fuels unless granted protection from the considerable tax levies applied to the latter. In the absence of tax relief, there is a need to explore alternate feedstocks for the production of biodiesel.

The processing of oilseeds for the production of edible vegetable oils generates by-product streams containing triglycerides, phospholipids and free fatty acids. In many cases these streams are of considerably lower value than the finished oil. Successful development of a scheme for ester synthesis from low-value lipids could address the economic barriers to a wider adoption of biodiesel [29].

Fatty acid methyl ester could be produced from tall oil, a by-product in the manufacture of pulp by the Kraft process. Tall oil consists of free C_{18} unsaturated fatty acids, resin acids and relatively small amounts of unsaponifiables. The fatty acid fraction of tall oil contains mainly oleic acid, linoleic acid and its isomers. Tall oil fatty acids are easily converted into their methyl esters by reaction with methanol in the presence of sulphuric acid, whereas the resin acids are virtually unesterified. Fatty acid methyl esters and resin acids were recovered in the yields of 93 and 94%, respectively, from esterified tall oil. Separation was accomplished by adding a solution of esterified tall oil in petroleum naphtha (80 to 180°C) used in the binary adsorption systems, through a column packed with molecular sieve 13X [36].

The cost of biodiesel can be reduced if we consider non-edible oils, used-frying

Table 11
Non-edible oil sources of India

Oil	Botanical name	Potential (million tonnes)	Utilised (million tonnes)	Percent utilisation
Rice-bran	Oryza sativa	474,000	101,000	21
Sal	Shorea robusta	720,000	23,000	3
Neem	Melia azadirachta	400,000	20,000	6
Karanja	Pongamia glabra	135,000	8000	6

oils and acid oils instead of edible oils. Non-edible oils such as neem, mahua, karanja, babassu, Jatropha, etc. are easily available in many parts of the world including India, and are very cheap compared to edible oils. The potential availability of some non-edible oils in India is given in Table 11 [7]. Used-frying oils are discarded by several countries including Netherlands, Germany, Belgium, Austria, United States of America and Japan. With the mushrooming of fast food centres and restaurants in India, it is expected that considerable amounts of used-frying oils will be discarded. These can be used for making biodiesel, thus helping to reduce the cost of water treatment in the sewerage system and generally assisting in the recycling of resources [37]. Acid oil, which is cheaper than both raw and refined oils, is a major by-product of the alkali refining industries and is a potential raw material for making biodiesel [38].

7. Conclusions

Alternate fuels for diesel engines have become increasingly important due to decreasing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. A number of studies have shown that triglycerides (vegetable oils/animal fats) hold promise as alternative fuels for diesel engines. However, the high viscosity, low volatility and poor cold flow properties of triglycerides, which result in severe engine deposits, injector coking and piston ring sticking, have prevented triglycerides from being used directly in diesel engines. One way to improve the fuel properties of triglycerides is the catalytic transesterification of triglycerides with alcohols to form monoalkyl esters of long-chain fatty acids, known as biodiesel which is quite similar to hydrocarbon-based diesel fuels in its main characteristics and provides similar engine performance with attractive emission levels.

From the reported literature on biodiesel, several conclusions have been recognized as valid. These include:

- conventional diesel engines can be operated without much, if any, modification on biodiesel;
- biodiesel can be used pure or in a mixture with hydrocarbon-based diesel fuels;
- biodiesel is nontoxic, safe to handle and biodegradable;
- no evaporation of low-boiling components takes place;

- exhaust gas is free of SO_2 and halogens;
- there is substantial reduction of soot, unburnt hydrocarbons, and also of carbon monoxide (when an oxidation catalyst is used) in the exhaust gases;
- NO_x emissions increase slightly if there are no changes in the engine setting;
- good performance in auto-ignition of fatty esters results in a smooth running diesel engine;
- biodiesel consumption is similar to hydrocarbon-based diesel fuels.

References

[1] Hobson GD, editor. Modern Petroleum Technology, 5th ed. Chichester: Wiley, 1984 Part II.

[2] Pipenger G. Making 'premium' diesel fuel. Hydrocarbon Processing 1997;76(2):63–78.

[3] LePera ME. Fuel quality vs engine types. Hydrocarbon Processing 1982;61(1):139–42.

[4] SEA News Circular. The Solvent Extractors Association of India, Vol. X, 1996.

[5] Marckley KS. Fatty Acids, 2nd ed. New York: Interscience, 1960.

[6] Goering CE, Schwab AW, Daugherty MJ, Pryde EH, Heakin AJ, Fuel properties of eleven vegetable oils, Trans. ASAE 1982;1472–1483.

[7] Kapur JP, Bhasin SD, Mathur KC. Oilseeds for food and industrial applications. Chemical Age of India 1982;33(9):475–82.

[8] Ali Y, Hanna MA, Cuppett SL. Fuel properties of tallow and soybean oil esters. J Am Oil Chem Soc 1995;72(12):1557–64.

[9] Rao PS, Gopalakrishnan KV. Vegetable oils and their methylesters as fuels for diesel engines. Indian Journal of Technology 1991;29(6):292–7.

[10] Ziejewski M, Kaufman KR, Pratt GL. Vegetable oil as diesel fuel. Seminar II, Northern Regional Research Center, Peoria, Illinois, 19–20 October, 1983.

[11] Schwab AW, Dykstra GJ, Selke E, Sorenson SC, Pryde EH. Diesel fuel from thermal decomposition of soybean oil. J Am Oil Chem Soc 1988;65(11):1781–5.

[12] Bagby MO. Vegetable oils for diesel fuel: opportunities for development. International Winter Meeting of the ASAE, Hyatt Regency Chicago, 15–18 December, 1987.

[13] Schwab AW, Bagby MO, Freedman B. Preparation and properties of diesel fuels from vegetable oils. Fuel 1987;66:1372–8.

[14] Otera J. Transesterification. Chem Rev 1993;93(4):1449–70.

[15] Krawczyk T. Biodiesel-alternative fuel makes inroads but hurdles remain. INFORM 1996;7(8):800–15.

[16] Freedman B, Butterfield RO, Pryde EH. Transesterification kinetics of soybean oil. J Am Oil Chem Soc 1986;63(10):1375–80.

[17] Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil Chem Soc 1997;74(11):1457–63.

[18] Feuge RO, Gros AT. Modification of vegetable oils. VII. Alkali catalyzed interesterification of peanut oil with ethanol. J Am Oil Chem Soc 1949;26(3):97–102.

[19] Dunn RO, Bagby MO. Low-temperature properties of triglyceride-based diesel fuels: transesterified methyl esters and petroleum middle distillate/ester blends. J Am Oil Chem Soc 1995;72(8):895–904.

[20] Chang DYZ, Van Gerpen JH, Lee I, Johnson LA, Hammond EG, Marley SJ. Fuel properties and emissions of soybean oil esters as diesel fuel. J Am Oil Chem Soc 1996;73(11):1549–55.

[21] Hui YH, editors. Bailey's Industrial Oils Fats: Industrial and Consumer Non Edible Products From Oils and Fats, 5th ed. Wiley-Interscience New York, 1996. 5.

[22] Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. J Am Oil Chem Soc 1984;61(10):1638–43.

[23] Fillieres R, Benjelloun-Mlayah B, Delmas M. Ethanolysis of rapeseed oil: quantitation of ethyl

esters, mono-, di-, and triglycerides and glycerol by high performance size-exclusion chromatography. J Am Oil Chem Soc 1995;72(4):427–32.

[24] Krisnangkura K, Simamaharnnop R. Continuous transmethylation of palm oil in an organic solvent. J Am Oil Chem Soc 1992;69(2):166–9.

[25] Formo MW. Ester reactions of fatty materials. J Am Oil Chem Soc 1954;31(11):548–59.

[26] Mittelbach M. Lipase catalysed alcoholysis of sunflower oil. J Am Oil Chem Soc 1990;67(3):168–70.

[27] Linko Y-Y, Lamsa M, Huhtala A, Linko P. Lipase-catalysed transesterification of rapeseed oil and 2-ethyl-1-hexanol. J Am Oil Chem Soc 1994;71:1411–4.

[28] Mukesh D, Banerji AA, Bevinakatti HS. A note on transesterifications of vegetable oils catalysed by lipase in a packed tubular reactor. Indian Chem Engr (Sec A) 1994;36(4):193–6.

[29] Haas MJ, Scott KM. Diesel fuel as a solvent for the lipase-catalysed alcoholysis of triglycerides and phosphatidylcholine. J Am Oil Chem Soc 1996;73(11):1497–504.

[30] Varese R, Varese M. Methyl ester biodiesel: opportunity or necessity. INFORM 1996;7(8):816–24.

[31] Clark SJ, Wagner L, Schrock MD, Piennaar PG. Methyl and ethyl soybean esters as renewable fuels for diesel engines. J Am Oil Chem Soc 1984;61(10):1632–8.

[32] Lee I, Johnson LA, Hammond EG. Use of branched-chain esters to reduce the crystallization temperature of biodiesel. J Am Oil Chem Soc 1995;72(10):1155–60.

[33] Lee I, Johnson LA, Hammond EG. Reducing the crystallization temperature of biodiesel by winterizing methyl soyate. J Am Oil Chem Soc 1996;73(5):631–6.

[34] Dunn RO, Shockley MW, Bagby MO. Improving the low temperature properties of alternative diesel fuels: vegetable oil-derived methyl esters. J Am Oil Chem Soc 1996;73(10):1719–28.

[35] Bondioli P, Gasparoli A, Lanzani A, Fedeli E, Veronese S, Sala M. Storage stability of biodiesel. J Am Oil Chem Soc 1995;72(6):699–702.

[36] Ustun G. Separation of fatty acid methyl esters from tall oil by selective adsorption. J Am Oil Chem Soc 1996;73(2):203–10.

[37] Murayama T. Evaluating vegetable oils as a diesel fuel. INFORM 1994;5(10):1138–45.

[38] Ghosh S, Bhattacharya DK, Dey P. Acid oils as raw materials for biodiesel. J Oil Technol Assoc India 1998;30(1):8–9.